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INVESTIGATION OF THE DISSOCIATION CHEMISTRY OF -NF_2 COMPOUNDS

Quarterly Summary Report for
August through October 1962

TM-1383

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SUMMARY

Work during the first quarter on this phase of the contract* has consisted entirely of apparatus construction. Two different techniques, thermal dissociation and photolytic dissociation, are now being planned for the study of the dissociation chemistry of $-NF_2$ compounds. The thermal dissociation will be done by adiabatic compression of a gas mixture with detection of the resulting species by time-of-flight mass spectrometry. The apparatus has been completed but has not yet been tested. The photolytic dissociation will be studied by kinetic spectroscopy. The necessary equipment for producing high-intensity photolyzing flashes and lower-intensity spectroscopic source flashes at precise time intervals has been assembled and tested. Complications in the construction of flash tubes have been encountered and are being overcome.

INTRODUCTION

The high-energy propellant possibilities associated with the NF_2 group have led to the development of an extensive new field of chemistry. The synthetic possibilities of now-available reagents such as N_2F_4, NF_3, HNF_2, N_2F_2, etc. are suggested by the host of new compounds already prepared. It appears, however, that these and similar compounds could be more effectively exploited, both as high-energy oxidizers and as synthesis reagents, if more were known about their dissociation chemistry. It is known, for example, that N_2F_4 is in equilibrium with NF_2 radicals, and appreciable concentrations of NF_2 can be formed with only moderate heating (1). Mechanisms have been proposed for the subsequent participation of the NF_2 radical in reactions; however, the rate of dissociation of N_2F_4 is not known at various temperatures, nor is the rate of dissociation of the NF_2 radical known. One can conceive of situations where the desired chemistry is frustrated because thermal dissociation reactions take place more rapidly than displacement or addition reactions, and vice versa. Because of the potential importance of this class of compounds, it seems important to conduct research designed to give fundamental knowledge of the dissociation chemistry of the $-NF_2$ compounds.

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* Continuing work on the combustion of elemental boron, initiated under contract NOnr-1883(00), is covered in a separate report.

THERMAL DISSOCIATION EXPERIMENTS

The study of the rapid thermal dissociation of very reactive gases at elevated temperatures is beset with experimental complications. If heat is applied to the container or reactor wall, the gas will be heated nonuniformly, its decomposition is apt to be catalyzed by the hot wall, and the gas may even chemically react with the wall. To study the thermal dissociation of substances such as N_2F_4 or NF_3, the gas should be heated homogeneously, at a rate that is fast compared to the rate of dissociation, and in a manner that avoids or minimizes complicating side reactions. If the products or reaction intermediates are also quite reactive, analytical problems arise which further complicate the obtaining of accurate data.

The shock tube has the advantage of rapid, homogeneous heating and has been successfully used to study a number of high-speed, high-temperature reactions. If it were necessary to study the dissociation of $-NF_2$ compounds at temperatures of the order of 1000°K and above, the shock tube would be the technique of choice; however, it is thought that 1000° will be an upper limit in temperature in the initial studies, and this is about the lower limit for useful shock-tube research.

Mechanical compression, if carried out rapidly enough to be essentially adiabatic, will result in homogeneous heating of the gas just as in a shock tube. Similarly, the reactor walls will remain comparatively cool, and interaction of the walls with the dissociating gas will be minimized. The same constraints apply to adiabatic-compression experiments as apply to shock-tube experiments; viz., the time required for the heating should be fast as compared to the rate of the reaction under study, the rate of heat loss to the reactor walls, and the resultant drop in temperature. Adiabatic compression, however, is applicable only to the lower temperature regimes required.*

The device shown in Figures 1 and 2 is an adiabatic compression machine designed to attach to the Bendix time-of-flight mass spectrometer through the fast reaction cell. The reaction chamber is a cylinder 13/16 inch in diameter and 7 inches long, terminating in a pinhole leak into the ionizing section of the mass spectrometer. The gas in the chamber is compressed and heated

*W. Jost has discussed the application of adiabatic compression devices for the study of fast reactions in reference 2.

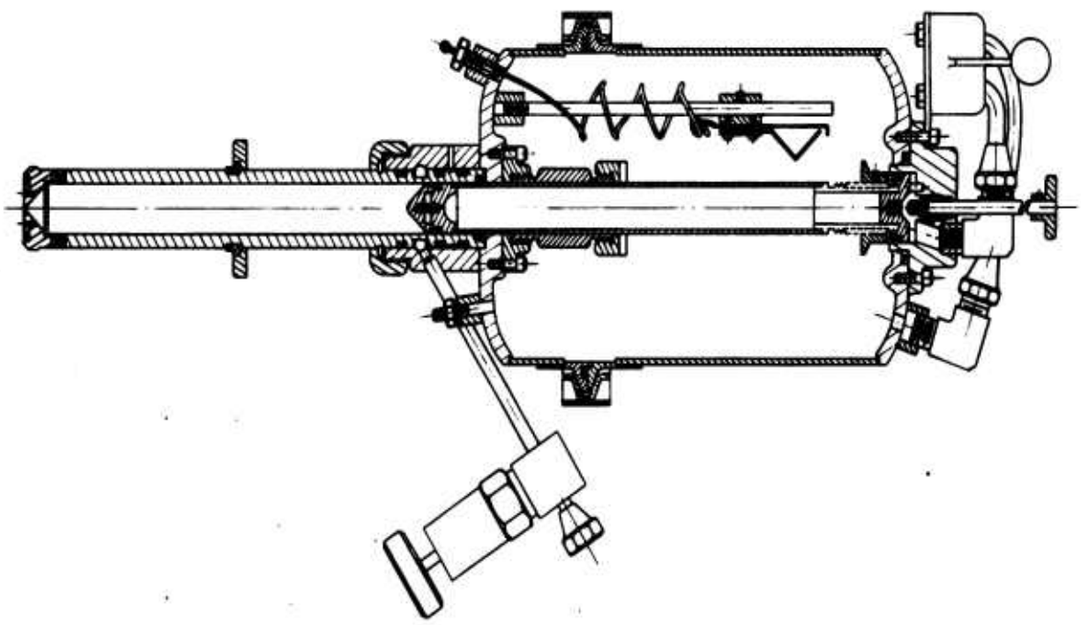
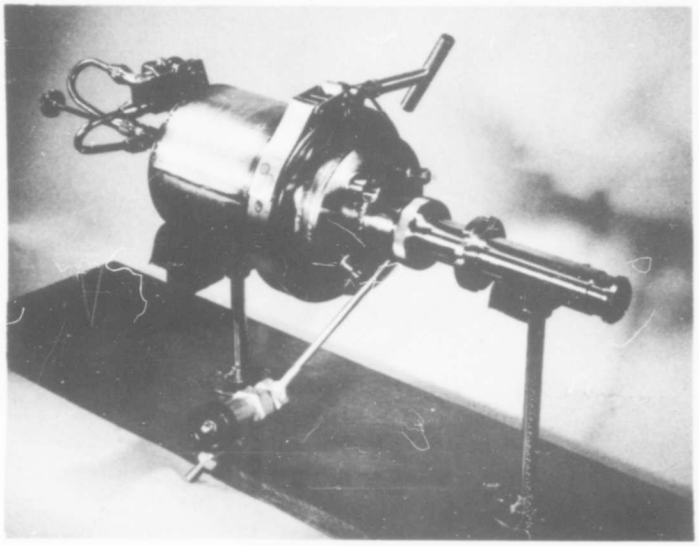


FIGURE I. ADIABATIC COMPRESSOR



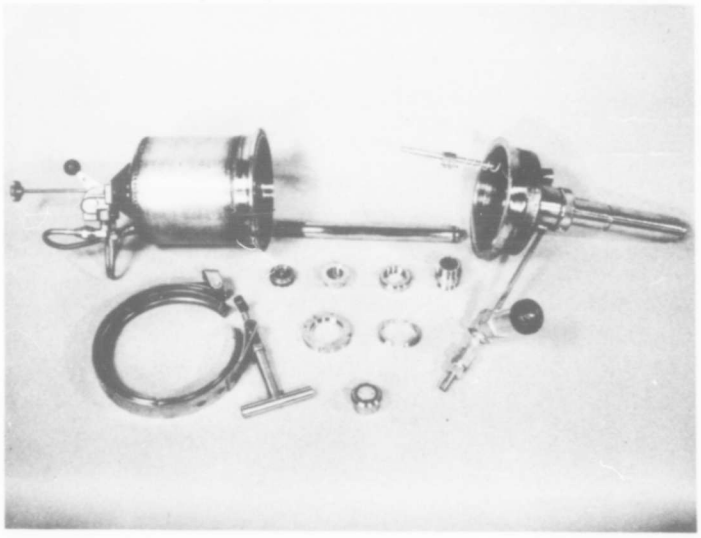


FIGURE 2. ASSEMBLED AND DISASSEMBLED VIEWS OF COMPRESSOR

by the gas-driven piston. It should be noted that if adiabatic compression occurs, an inert gas can be heated from 300 to 1000°K by reducing the volume to 14.3% of its original value, according to the relation

$$c_V \ln(T_2/T_1) = -R \ln(V_2/V_1)$$

It should be further noted that the temperature increase is independent of the initial pressure. Inasmuch, though, as a high initial pressure would permit increased heat transfer to the walls and hence cause a more rapid drop in the final temperature and, in addition, would make the compression more difficult, it is planned that the apparatus be used with initial pressures of the order of a few torr.

The planned experimental procedure is to prepare a reaction mixture of a percent or two of the $-NF_2$ compound and the remainder argon labeled with 1% krypton. The constant value of c_V for inert gases permits reasonably accurate calculations of the final temperature of the compressed gas (reasonable estimates can be made for the temperature correction necessary for the added $-NF_2$ compound). The use of an inert gas for the heating medium also permits higher temperatures with considerably less compression than if the pure reaction gas were used.

The 1% of krypton is added to the mixture for quantitative reference in the mass spectrometer. As the gas mixture is compressed, the leak rate into the mass spectrometer will increase and cause an increase in the intensity of the output signal. The krypton concentration will be of the same magnitude as the $-NF_2$ compound being studied. However, when the gas is heated, the $-NF_2$ compound will dissociate, and its mass spectra will change relative to the nondissociating krypton spectra. Mass spectra of the krypton and the dissociating $-NF_2$ compound will be displayed on an oscilloscope at 50-μsec intervals and photographed with a drum camera. The change in concentration of the species with time thus recorded permits the determination of the kinetics of the dissociation reaction.

Gases can also be heated homogeneously by absorption of radiant energy. In flash photolysis it sometimes happens that instead of the radiant energy directly activating a specific hand, the energy is absorbed and rapidly degraded to heat. The reaction is then followed by the technique of kinetic spectroscopy as described in the next section.

PHOTOLYTIC DISSOCIATION

The kinetics of photolytic dissociation are most conveniently studied by kinetic spectroscopy. This technique has been reviewed recently by R. G. W. Norrish (3). The absorption of radiant energy by a molecule can result in the raising of the molecule to an excited state which may be more reactive than the ground state, the breaking of specific bonds (depending on the wave length of the interacting photons), or the elevation of the temperature of the molecule. All three processes are of interest to us and, to the extent that the effects can be separated and controlled, should be separately studied.

It is first of all necessary that light be absorbed by the substances under study. Consequently NF_3 has been examined in a specially built quartz cell at pressures as high as 715 torr for an absorption spectrum from 2000 A through the visible, using the Jarrell-Ash plane-grating high-speed spectrograph. As a light source for the visible region an A. C. Pointolite was used, and for the ultraviolet region a hydrogen uv source from a Beckman D. U. Spectrophotometer was used. A careful examination of the resulting plates, both visually and from microphotometer traces, showed no evidence of any absorption in this region of the spectrum.

The absence of an electronic absorption spectrum above 2000 A indicates that direct flash photolysis of the NF_3 is unlikely to occur with quartz equipment in air. It has therefore been decided that a sensitizer gas be used, making use of a process of the type:

$$A + h\nu \rightarrow A^*$$

$$A^* + NF_3 \rightarrow A + NF_2 + F$$

such that $E(A^*) - E(A) > D(F_2N - F)$ for NF_3.

Even if such a process does not occur, it may be possible to achieve "flash heating" under appropriate conditions. An examination of possible sensitizer gases indicates that NO is perhaps the best compromise, at least for initial experiments. The expectation is that any reaction of NO with NF_3 or NF_2 would be slow compared with the dissociation reaction. The inert monatomic gases do not absorb in an accessible region and so cannot be used as sensitizers.

Other $-NF_2$ compounds to be studied, such as HNF_2 or N_2F_4 have not yet been examined to see if they absorb in an accessible region of the spectrum. If it

is found that they do not, similar considerations in the choice of a sensitizer would also apply to them.

The electronic equipment for the flash-photolysis device has been constructed. Circuit diagrams for the charging equipment and the time-delay mechanism are shown in Figures 3 through 6. In design we are trying to duplicate the apparatus described by Calloman and Ramsay (4). The 40-μf capacitor should be capable of delivering up to 2000 joules in a time of about 20 μsec.

Flash tubes have been constructed with a modification of a design presented by Claesson and Lindqvist (5). Heavy tungsten electrodes were sealed into quartz tubes with Araldite epoxy resin, and the tubes were filled with xenon to a pressure of 75 torr. Sample cells and flash tubes are both 25 cm long. The electrode design is shown in Figure 7.

In the course of checking the equipment, a number of difficulties have been encountered. The 40-μf capacitor was found to be defective and had to be returned for repair. Slight modifications were found to be desirable in the high-voltage charging apparatus for the safety of the operators. A further complication was the very nerve-racking experience of having the flash tubes explode when fired. Private communications with Ramsay revealed that this was perfectly normal until the proper operating parameters were established. All of these difficulties have now been overcome, and final checkout on procedures is under way.

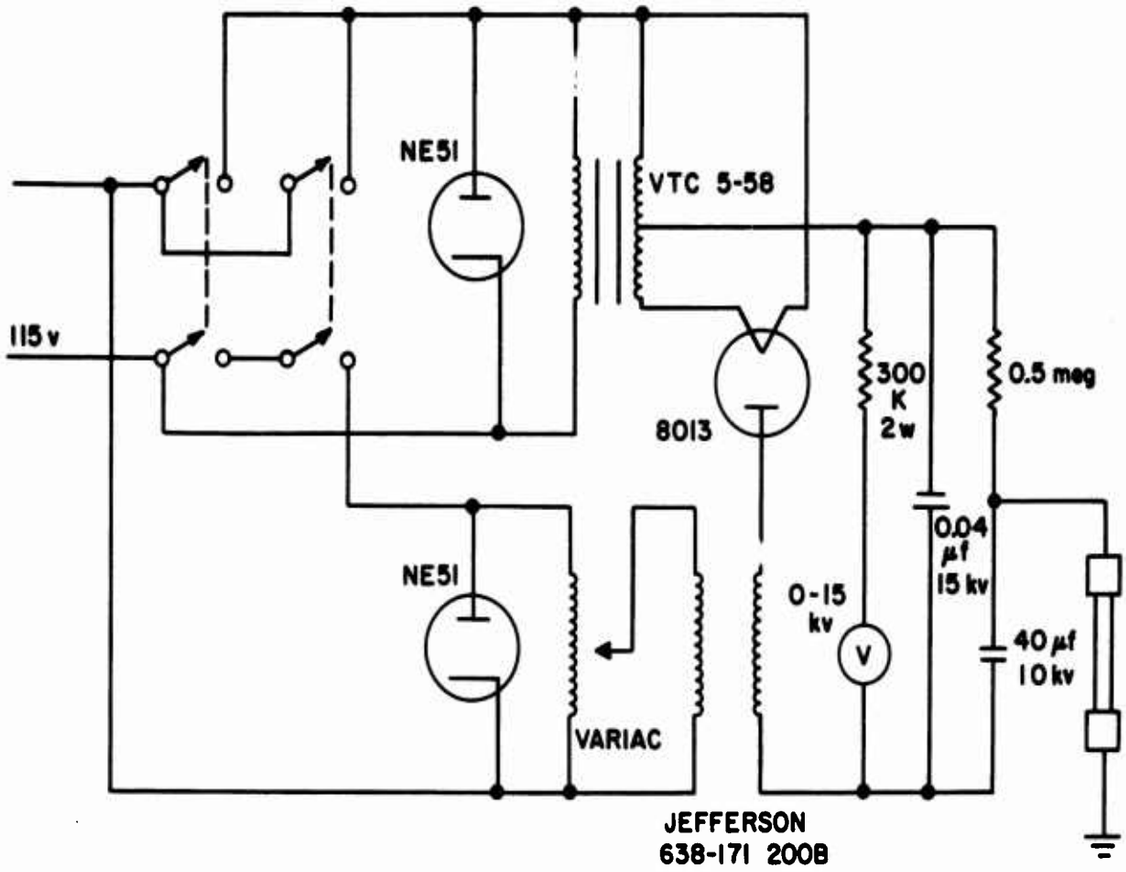


FIGURE 3. PHOTOLYSIS FLASH CHARGING CIRCUIT

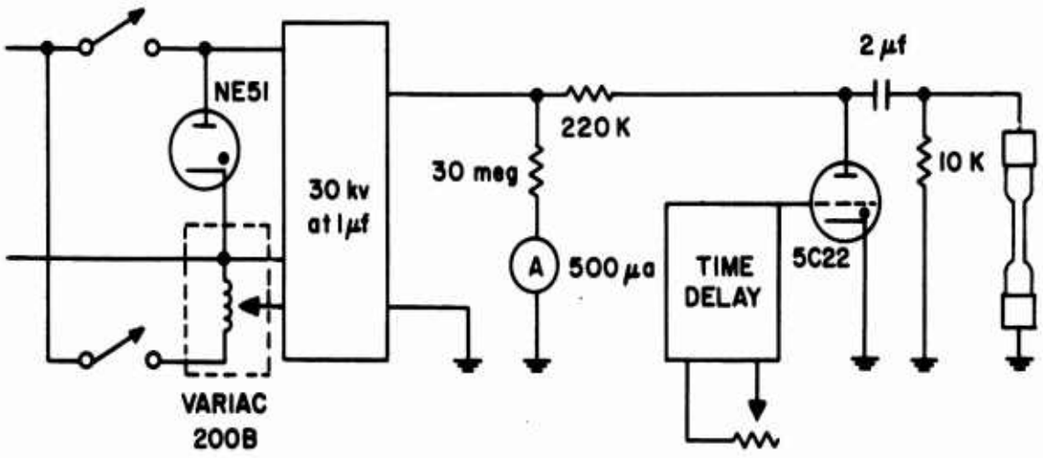


FIGURE 4. SOURCE FLASH CHARGING CIRCUIT

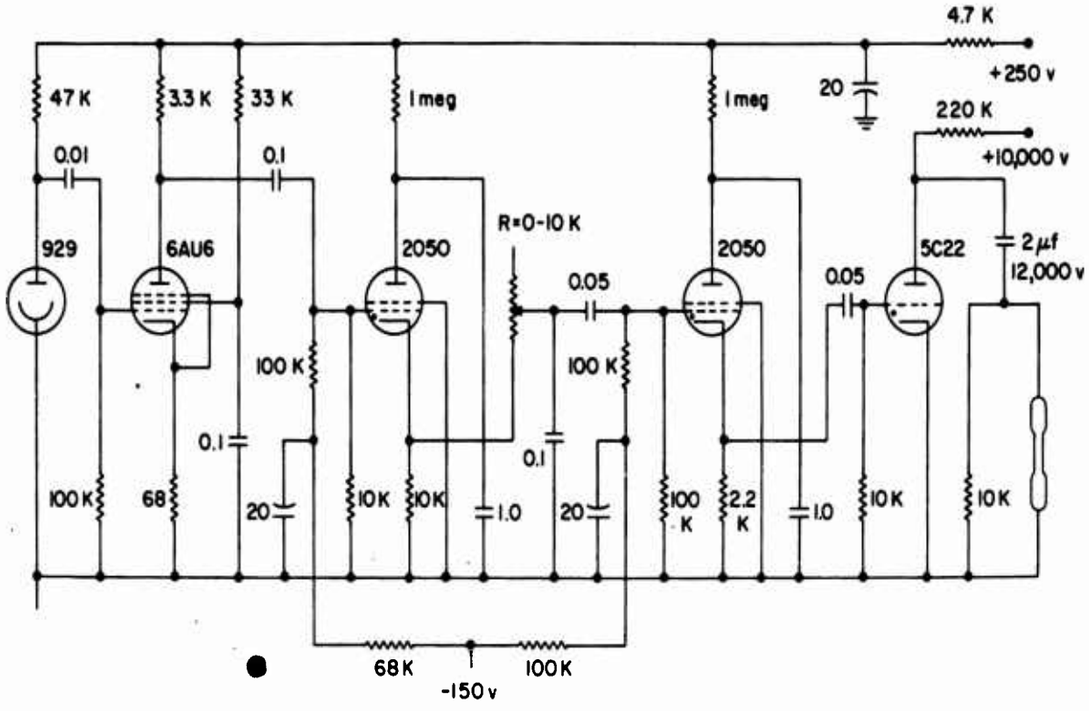


FIGURE 5. CIRCUIT FOR CONTROLLING THE TIME DELAY BETWEEN THE PHOTOLYSIS AND THE SOURCE FLASHES

CAPACITORS IN MICROFARADS

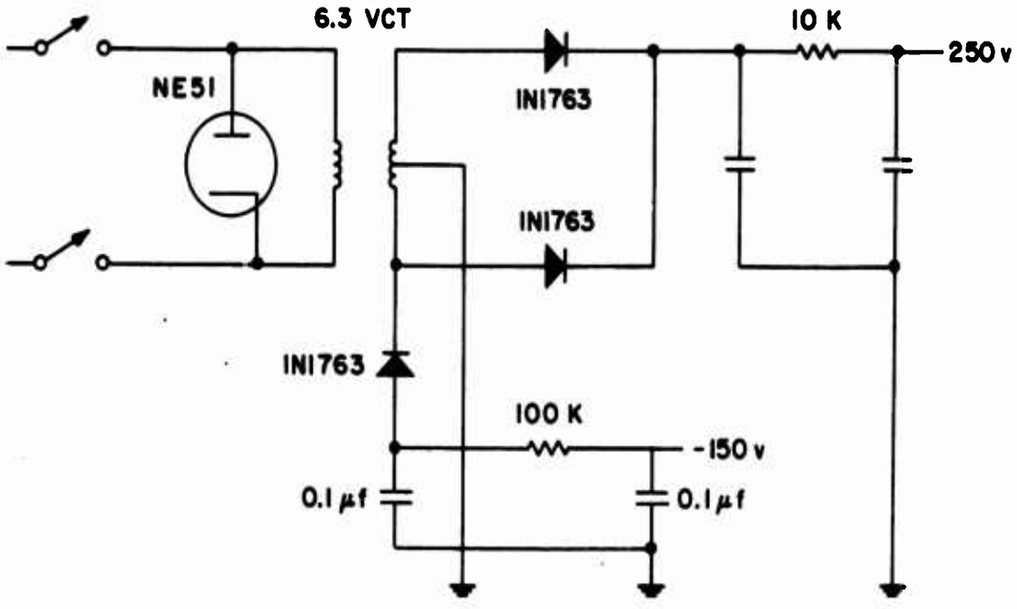
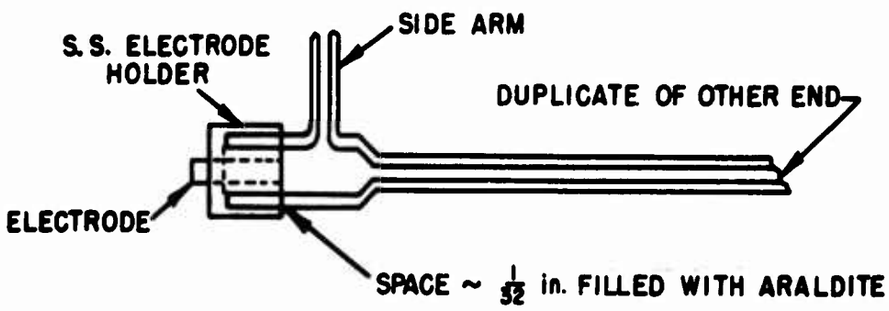
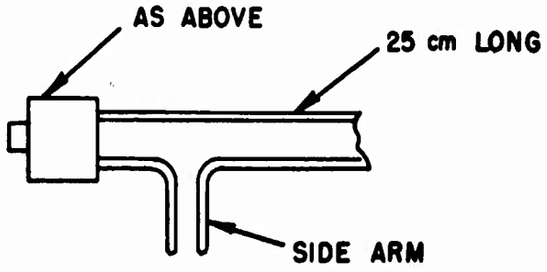


FIGURE 6. TIME-DELAY POWER SUPPLY

APPROX. $\frac{1}{2}$ SCALE



SOURCE LAMP



FLASH LAMP

FIGURE 7. ELECTRODE DESIGN

FUTURE WORK

Work is commencing on the checkout of the adiabatic compression apparatus. This will involve the determination of the compression speed and the establishment of proper driving gas pressures. The apparatus must be mated to the mass spectrometer, and suitable chamber pressures must be established to give a usable leak rate into the mass spectrometer. Actual kinetic experiments with this apparatus will necessarily be delayed until the Beckman and Whitley drum camera for recording the oscilloscope output is received in December.

The flash-photolysis kinetic-spectroscopy experiments will be started very shortly. In addition, the absorption spectra of other $-NF_2$ compounds of interest, e.g., HNF_2 and N_2F_4, will be determined as soon as it is convenient.

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(3) R. G. W. Norrish, Am. Scientist, 50, 131 (1962).

(4) J. H. Calloman and D. A. Ramsay, Can. J. Phys., 35, 129-133 (1957).

(5) S. Claesson and L. Lindqvist, Arkiv Kemi, 11, 535 (1957).

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